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Toward The Synthesis of Functionalized Poly (Ether Ether Ketone): Monitoring the meta-Fluorine Displacement in 3,5,4'-trifluorobenzophenone

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TOWARD THE SYNTHESIS OF FUNCTIONALIZED, SEMI-CRYSTALLINE POLY (ETHER ETHER KETONE): MONITORING THE META-FLUORINE DISPLACEMENT IN 3,5,4'-TRIFLUOROBENZOPHENONE

A thesis submitted in partial fulfillment

of the requirements for the degree of Master of Science

By:

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B.S. Loras College, 2013

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GRADUATE SCHOOL

May 18th, 2017

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY **Giovanni Covarrubias** ENTITLED **Toward The Synthesis of Functionalized Poly (Ether Ether Ketone)s: Monitoring the meta-Fluorine Displacement in 3,5,4'-trifluorobenzophenone** BE ACCEPTED IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF **Master of Science.**

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ABSTRACT

Covarrubias, Giovanni. M.S., Department of Chemistry, Wright State University, 2017. Toward The Synthesis of Functionalized Poly (Ether Ether Ketone): Monitoring the meta-Fluorine Displacement in 3,5,4'-trifluorobenzophenone

The synthesis of functionalized, linear poly (ether ether ketone), tailored to be semi-crystalline and soluble in a variety of organic-solvents was explored. Nucleophilic aromatic substitution was a chemical reaction method used to condense 3,5,4'-trifluorobenzophenone (TFK) with four different phenols at its *para*-positioned carbon-fluorine site: 4-methoxyphenol, 3-aminophenol, 4-bromophenol, and *m*-cresol. Further poly-condensation of functionalized TFK occurred at the *meta*-positioned carbon-fluorine sites with 4,4'-Bis[4-hydroxyphenoxy] benzophenone (Big A_2) and 4,4'-difluorobenzophenone at molar equivalents of 1 to 0.5, respectively. The reaction afforded products that became insoluble in solvents needed for nuclear magnetic resonance spectroscopic (e.g. DMSO-d_6) analysis. The lack of desirable compounds compelled the necessity of examining the displacement of the fluorine groups in TFK located *meta* to the electron withdrawing group, the carbonyl moiety. Gas Chromatography/Mass Spectrometry (GC/MS) and Nuclear Magnetic Resonance Spectroscopy (NMR), ^{1}H and ^{13}C, were used to analyze samples at varying reaction times and revealed that while it is possible to displace at least one of the meta-fluorine atoms in mono-substituted TFK with Big A_2 and Bisphenol A, more time and a potentially higher temperature may be needed to complete the reaction. The synthesis of 75:25 PEEK-co-*meta*-PEEK, **5**, from a previous project was successfully replicated and verified using Differential Scanning Calorimetry (DSC).

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ACKNOWLEDGMENT

I wish to thank Dr. Fossum for his assistance in my chemical research project for nearly four years. His acceptance of me into his laboratory has given me the opportunity to observe and perform reactions using the knowledge that I have gained as a student of chemistry/biochemistry during my undergraduate and graduate years of higher education. I would also like to thank the Fossum Research Group and friends for their advice in exploring better methods and other questions related to my project. I also thank Dr. William Feld and Dr. Daniel Ketcha for being part of my committee members for my thesis defense. Wright State University and faculty members deserve a special gratitude for letting me take their classes, become a teacher's assistant, and allowing me to further continue my interest in the science of chemistry. Finally, I would like to thank my family for their support during my time at Wright State.

INTRODUCTION

Beginning in the 1950's, the development and examination of poly (arylene ethers), **PAEs**, a type of high performance engineering thermoplastic, gained attention for potential use in the aerospace and electronics industries.[1,2] At high temperatures, these materials generally retain their excellent mechanical properties, thermal stability, and resistance to organic solvents, hydrolysis and degradation.[3,4,5]

For decades, these compounds have been applied to create aerospace, automobile, nuclear reactor, and electronic components, coatings, labels, membranes, insulators, moldings, and reinforcements.[2] Three general groups of **PAEs** exist that contain varying functional groups, which influence their physical and chemical properties: poly (aryl ether sulfones), **PAES**, poly (ether imides), **PEI**, and poly (aryl ether ketones), **PAEK**.[2]

Due to a high resistance to solvents, **PAEs** are often difficult to synthesize and be utilized in the industry. As such, there is an increasing amount of research and development introducing different types of functional groups that alter their properties in a desired manner for a specific purpose.[6-13] **PAEs** have been successful in being tailored by introducing various functional groups, but further modification may be necessary to keep certain properties of the compounds consistent while muting others that prevent it from being analyzed properly.

1.1 Poly Arylene Ethers (PAE)

As shown in **Figure 1**, the general structure of **PAE** is best described as an aromatic hydrocarbon repeating unit containing ether linkages and electron-withdrawing groups within the backbone.[2,3]

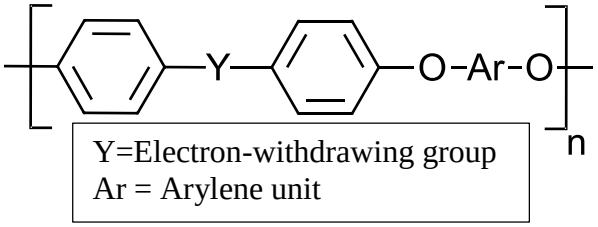


Figure 1: Structure of a PAE[2]

These electron-withdrawing groups are often made up of carbonyls, sulfonyls, and imides that affect properties such as glass transition temperature, solubility, and crystallinity of the polymers. Specifically, while **PAES** and **PEI** are amorphous compounds (with the exception of at least one type of PEI), **PAEK** maintain a high amount of semi-crystallinity and their imperviousness to acidic solvents.[2] **PEI** may be amorphous but are also resistant to common organic solvents.[17] Apart from these three groups, there remains one other type whose origin is defined as a precursor in the synthesis of the majority of **PAE**, named poly(phenylene oxide), **PPO**, as depicted in **Figure 2**.

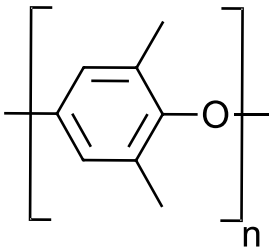


Figure 2: Structure of PPO

The simplest types of **PAE**, poly(phenylene oxide)s, **PPO**, have been known since 1916 by Hunter et al., and commercially synthesized since the 1950's by oxidative coupling using di-substituted phenols with substituents *ortho* to the hydroxyl group, a copper halide catalyst, and an amine base in the presence of oxygen gas.[14,15]

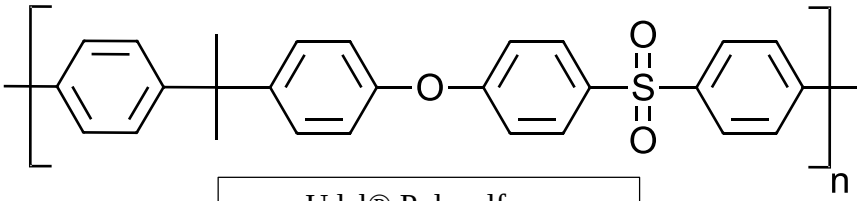
PPO is characterized by maintaining low creep, high modulus, and low water absorption at high temperatures; while still having hydrolytic stability, excellent dielectric and mechanical properties over a range of temperatures between -40°C to over 150°C.[16] However, they are amorphous materials with poor solvent resistance.

1.2 Poly Arylene Ether Sulfones (PAES)

PAES are a group of thermoplastics that possess aryl groups linked by ether bonds and sulfone groups. They possess high thermostability at temperatures around 260°C, are chemically stable, highly resistant to hydrolysis and oxidation due to a lack of aliphatic groups, have high glass transition temperatures, and are soluble in common organic solvents, such as NMP, DMSO, and THF.[18]

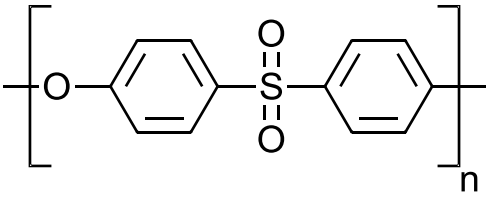
These sulfone-containing polymers (**Figure 3**) were synthesized as a commercial product by Union Carbide Corporation as Udel® Polysulfone in 1965 but its repeating unit contained a bisphenol A co-monomer. A second commercial product of **PAES** was

synthesized and distributed by the Imperial Chemical Industries in the UK during the 1980's and was marketed as polyethersulfone 200 P™.[19]



Udel® Polysulfone

T_g = 185°C



ICI's Polyether Sulfone 200 P™

T_g = 230°C

Figure 3: Commercial examples of polyethersulfones

With a glass transition temperature of ~220°C, **PAES** are generally known for their high strength/stiffness, good hydrolytic stability, high deflection temperatures, transparency, ease of melt fabrication, good colorability, and good dielectric properties over a broad range of temperature.[19] Despite these properties, their low-resistance to solvents make them difficult to use in applications where acidic environments are present.

1.3 Poly Ether Imide (PEI)

PEI are composed of polyimides that are synthesized from the fusion of a dianhydride and diamine, which contain ether linkages within its backbone.[20] In general, these amorphous polymers are characterized by their high temperature resistance, high tensile strength, flame resistance, transparency, resistant to some solvents, and low smoke emission.[21] One type of **PEI**, ULTEM®, is not amorphous and exhibits a melting temperature of 426°C. The compounds have been used in applications such as aerospace materials, microelectronics, and membranes for the separation of gases. However, they can be insoluble in some common halogenated solvents, become thermally and hydrolytically unstable, and water-emerging as a by-product from imidization can also form voids in bulk materials.[17,20] **Figure 4** shows an example of a PEI used in industry.

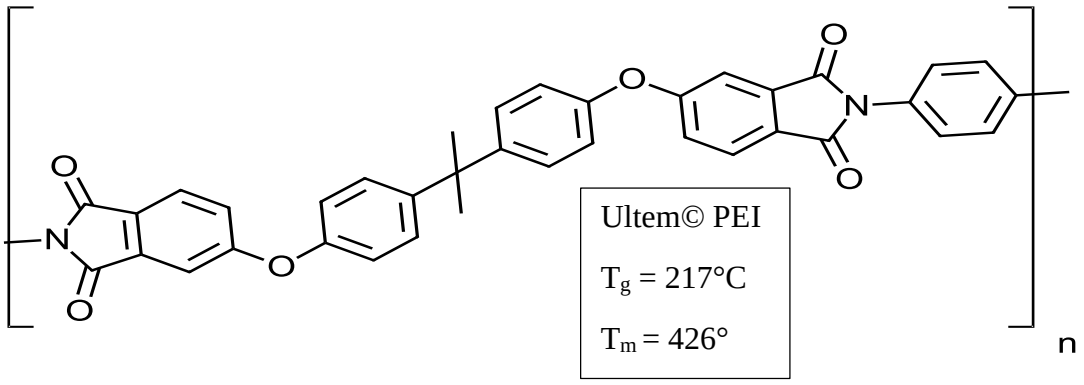


Figure 4: Commercial example of a polyetherimide

1.4 Poly Arylene Ether Ketones (PAEK)

PAEK are engineering thermoplastics that contain phenyl rings and carbonyl groups within their backbone. Most are semi-crystalline, have a glass temperature range of 140-180°C, melting points between 330-390°C, have low-smoke emission, and are highly

resistant to acidic environments.[23] Their properties make them valuable to use in applications such as matrix resins for reinforced composites, films, coatings and medical tools.[24,25] Within this group, a number of variations of **PAEK** exist whose number of ketones and ether linkages change their physical and chemical properties. Examples in **Figure 5** include poly ether ketone (PEK), poly ether ether ketone (PEEK), poly ether ketone ether ketone ketone (PEKEKK), and poly ether ketone ketone (PEKK).[26,27]

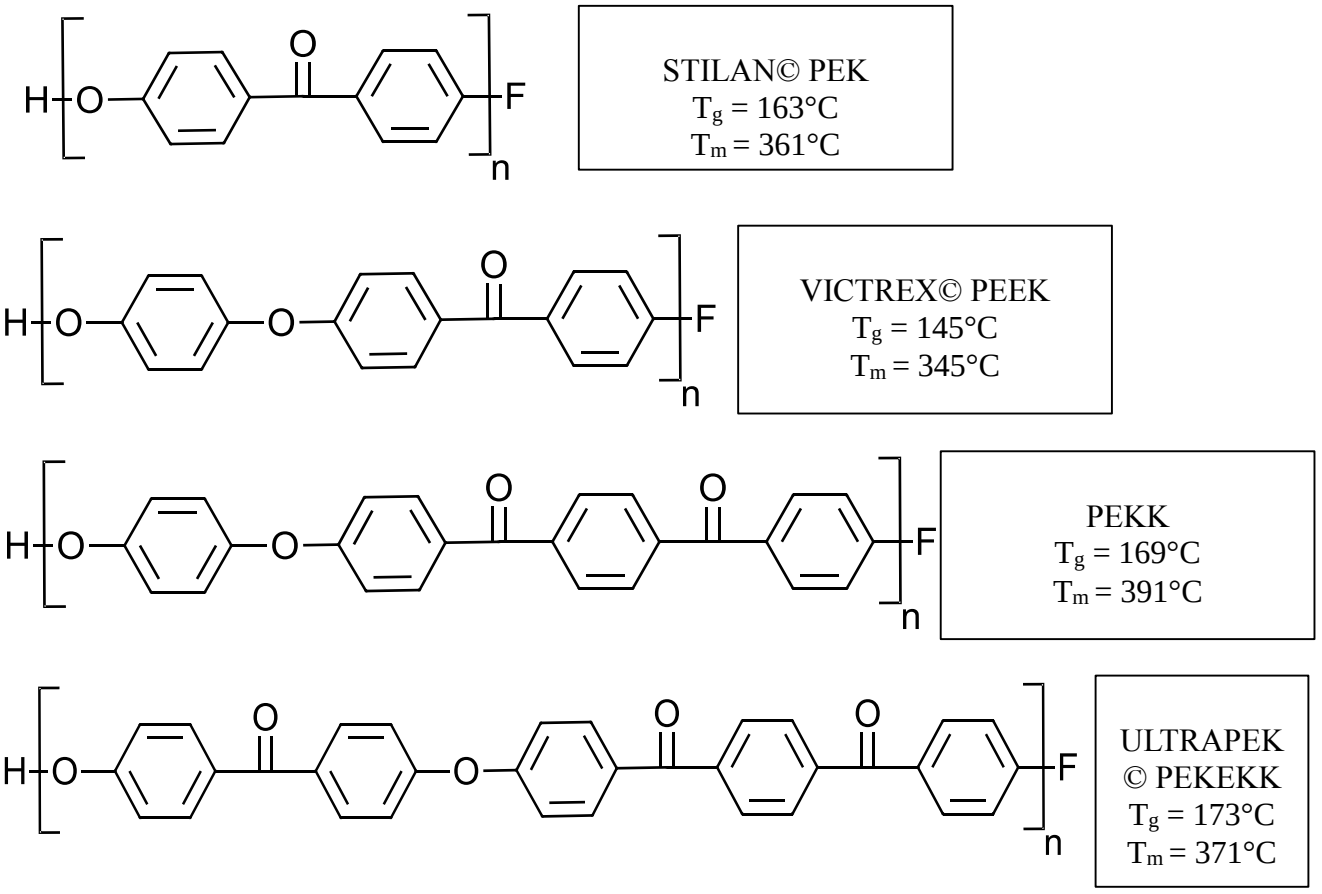


Figure 5: Commercial examples of PAEKs

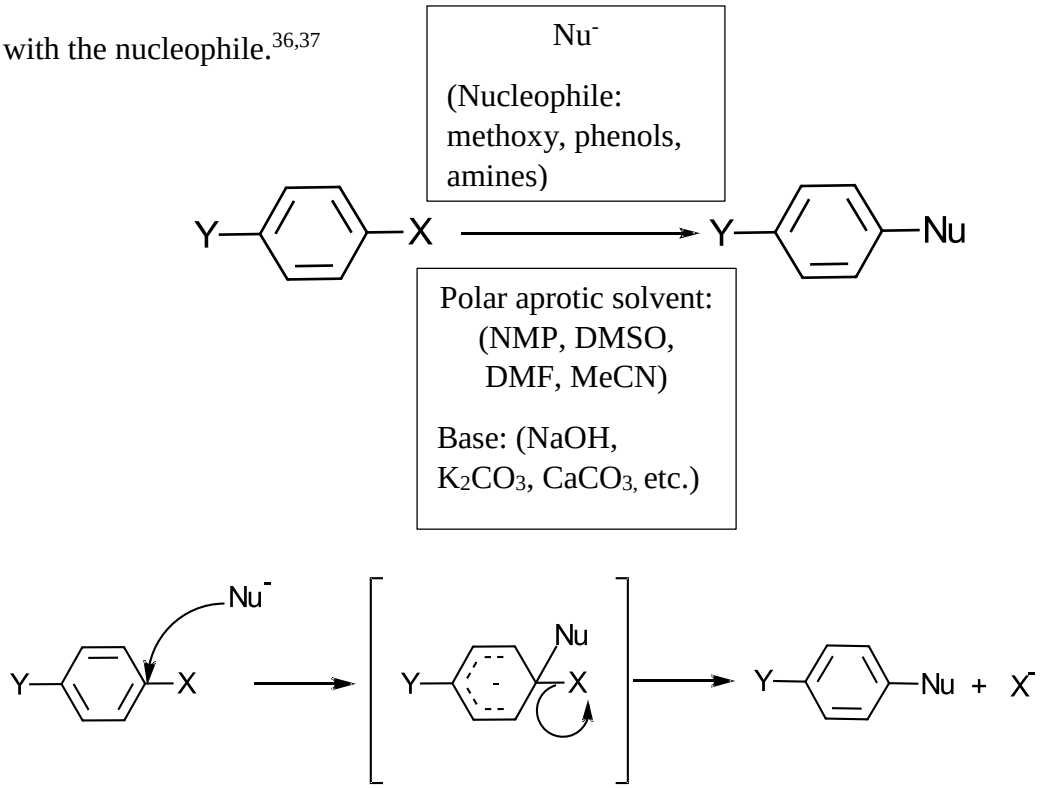
1.5 Poly Ether Ether Ketones (PEEK)

A subset of PAEK, **PEEK** is a linear, semi-crystalline, high temperature resistant, anti-oxidative compound, insoluble in common organic solvents, with low flammability, low toxic gas emission, and biologically inert thermoplastic. With a glass transition temperature of 145°C and melting temperature of 343°C, these excellent mechanical and chemical properties make it useful in applications involving automobile, aerospace, and medical industries.[28,29,30,31] **PEEK** is the most commonly used PAEK to undergo experimentation and analysis, producing derivatives that alter its properties to conform to a specific application needed for industrial and academic use.[32,33,34,35]

1.6 Synthesis of PAEs via Nucleophilic Aromatic Substitution (NAS)

PAES and PAEK are synthesized by one of two routes: Electrophilic aromatic substitution or nucleophilic aromatic substitution. The former is usually done via a Friedel-Crafts acylation, while the latter is performed using a halogenated aromatic monomer containing an electron-withdrawing group that activates the halides for displacement with phenoxide nucleophiles that are typically generated in the presence of a weak base and a polar aprotic solvent, at high temperatures.[2,24,30] **Scheme 1** shows that the initial process of NAS begins when an aryl dihalide contains an activating group, such as a sulfonyl or carbonyl compound, located ortho or para from the halogen atom. The activating group pulls electron density from the *ipso*-carbon containing the halide, designated as the leaving group. A nucleophile attacks the ipso-carbon, causing the ring to lose aromaticity and form a Meisenheimer complex, a type of resonance-stabilized carbanion. Aromaticity is

regained when the carbanion forces the halide leaving group out of the ring, replacing it with the nucleophile.[36,37]



Scheme 1: General reaction of Nucleophilic Aromatic Substitution

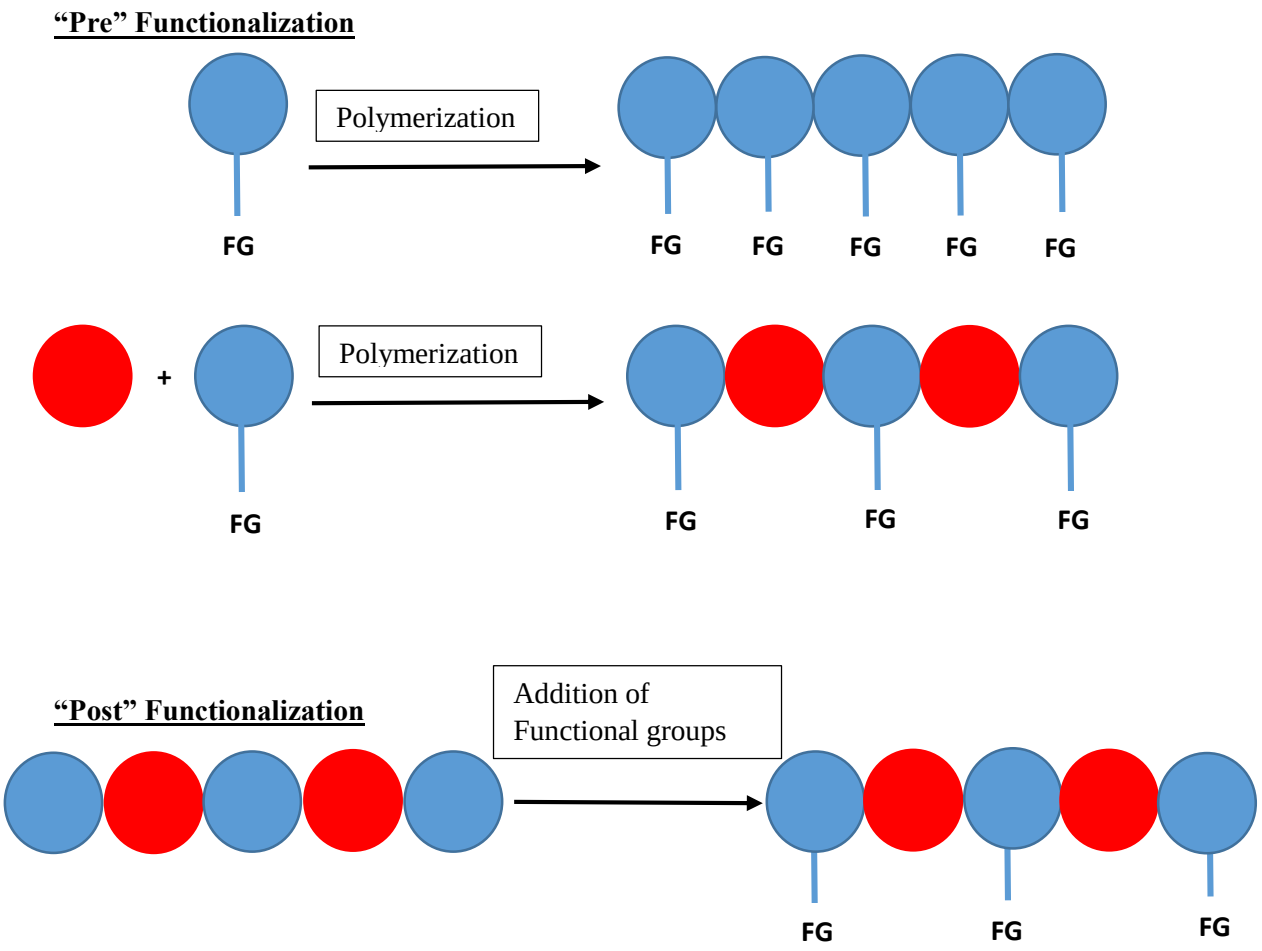
In recent years, it has been discovered that NAS does not *only* occur when the electron withdrawing group is located ortho or para to the halide group(s). Studies from Kaiti et al., Tienda et al., and van Beek revealed that PAE containing sulfonyl, phosphoryl, and carbonyl groups that are located *meta* to the halides are strong enough to decrease electron density on the ipso-carbon.[38,39,40]

1.7 Introducing Functionality to PAE

The idea of subjecting PAE to further modification without affecting their inherent qualities has been investigated for decades. By introducing varying functional groups to the polymers, called functionalization, the resulting products can be enhanced with additional properties and contain more sites of reaction to synthesize even more distinctive types of compounds, if needed.[41]

Many types of functional groups have already been studied and incorporated into the polymeric backbone, usually when activating electron-withdrawing groups are *para* to the site of reaction.[42-47] However, recent research has shown that substitution of the halide groups can occur even when activated from the *meta* sites position.[48] The resulting activating groups, which can carry functional groups, are pendent to the backbone. Functionalization can be achieved via two different pathways, one in which functional groups are introduced before polymerization occurs, "Pre", and the other where the functional groups are introduced after polymerization, "Post".

1.8 Synthesis of Polymers: "Pre" vs. "Post" Functionalization



Scheme 2: "Pre" Functionalization of Polymers compared to "Post" Functionalization

Both methods of functionalization via nucleophilic aromatic substitution have been used to alter the chemical and physical properties of polymers. However, each has advantages and disadvantages, depending on the reaction conditions and types of functional groups being used. Examining **Scheme 2** reveals that during pre-functionalization, the functional group can be introduced into the initial monomer. The

functionalized monomer can now polymerize with other similar monomers or completely different ones. The number of functional groups being added and their location before polymerization is more controllable. Drawbacks in using this method are that side reactions can possibly occur if unreacted monomer is still present during the reaction or if some functional group during polymerization is altered and the resulting polymers could be of low molecular weight due to the resulting changes in stoichiometry.[41]

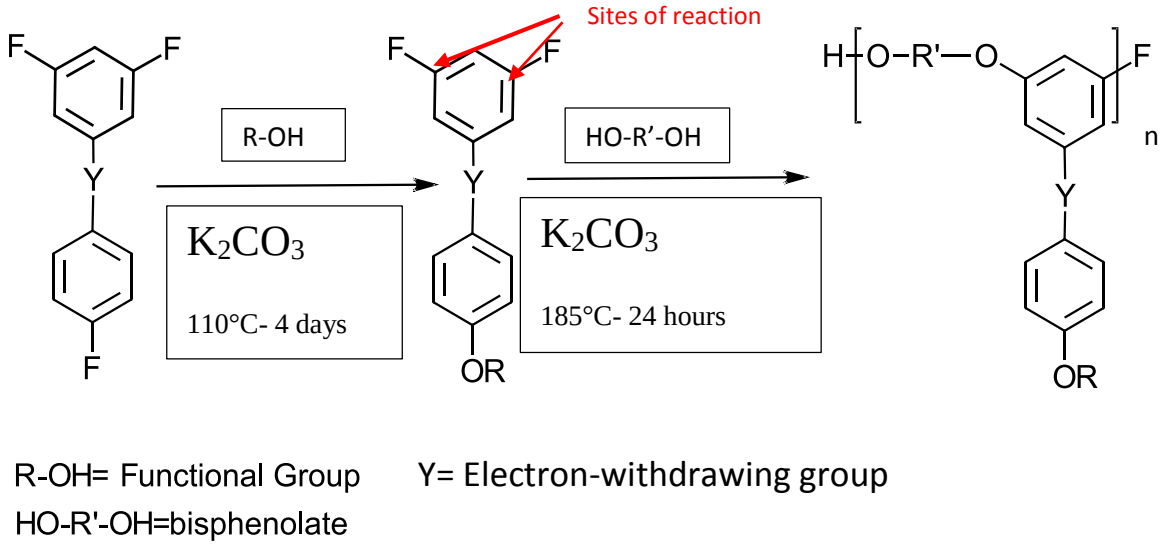
For post-functionalization, the addition of functional groups after polymerization is more varied since they can occur on rings containing electron-withdrawing groups or electron-donating groups. This ease of functionality, however, can alter the polymer's backbone via unwanted reactions, such as transetherification, and introduce significant changes to its chemical and physical properties.[41]

It is possible to design a reaction method that incorporates both types of functionalization. In a study done by Tatli et al., 3,5-difluoro-1-((3-iodophenyl sulfonyl)) benzene was synthesized and contained an iodo functional group. The compound underwent a condensation reaction with Bisphenol A, after which it was exposed to palladium-catalyzed cross-coupling reactions with phenyl, naphthyl, and 4-acetylphenyl boronic acids, as well as styrene, causing the iodo group to be replaced in order to synthesize the corresponding phenyl, naphthyl, 4-acetyl phenyl, and 2-phenylvinyl functionalized polymers.[49]

1.9 Tailoring Solubility and Crystallinity of Functionalized PAEK

Testing for the solubility of PAEK has revealed that these semi-crystalline polymers resist dissolving in common organic solvents unless strong acids are used. A study done by Fortney examined PEEK that was modified using different mol% of an isomeric *co*-monomer. A series of PEEK polymers were developed from two difluorinated benzophenone isomers (3,5 and 4,4') and a custom bisphenol that has a linear, PEEK-like structure. The results indicated that increasing the ratio of linear PEEK-like co-monomers to meta-PEEK structures lead to insoluble polymers in common, organic solvents such as dichloromethane, tetrahydrofuran, dimethyl formamide, DMSO, DMAC, NMP, and toluene. Not all of the polymers were amorphous, beginning with 25% of meta-PEEK to 10%, each of them had crystalline regions. One polymer whose mol% of linear PEEK vs. meta-PEEK was 75:25, respectively, contained an aromatic ring pendant to the backbone. Another fluorinated benzophenone, 3,5,4'-triflurobenzophenone, a similar compound to 3,5-difluorobenzophenone but with an extra fluorine para-positioned from the carbonyl group and located pendant to the backbone can serve as a site of functionalization (see **Scheme 3**).[50]

Previous research in our group has focused on functionalizing PAES and PAEK using 3,5,4'-trifluorodiphenylsufone and 3,5,4'-trifluorobenzophenone as starting monomers, respectively.[51,52] Using a method devised by Boakye called reactivity ratio controlled poly-condensation (RRCP), the *para*-positioned fluorine atom pendent to the polymeric backbone can be displaced via pre-functionalization, leaving two fluorinated carbons *meta* to the activating group that serve as sites of polymerization (**Scheme 3**).

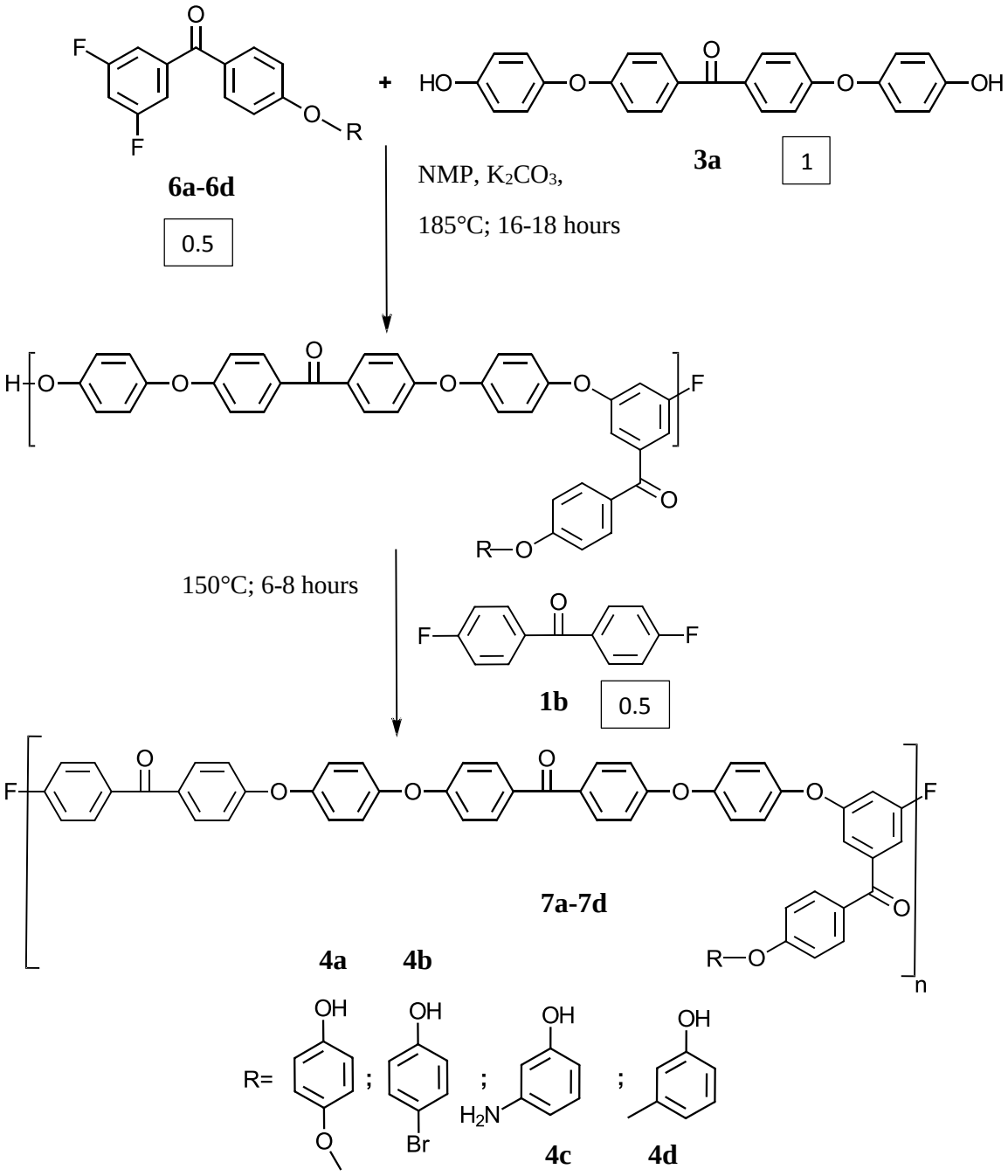


Scheme 3: General method of reactivity ratio-controlled poly-condensation (RRCP)

Difficulties arose in synthesizing polymers originating from trifluorodiphenylsulfones in which a mixture of unreacted monomer and its functionalized counterparts of both *para* and *meta*-functionalized isomers occurred. However, the trifluorobenzophenones were exclusively *para*-functionalized under the same reaction conditions. The PEEK analogues that were prepared were revealed to be amorphous with glass transition temperatures that ranged between 108°C-136°C. Therefore, the next logical step would be to investigate the synthesis of semi-crystalline analogues.[51]

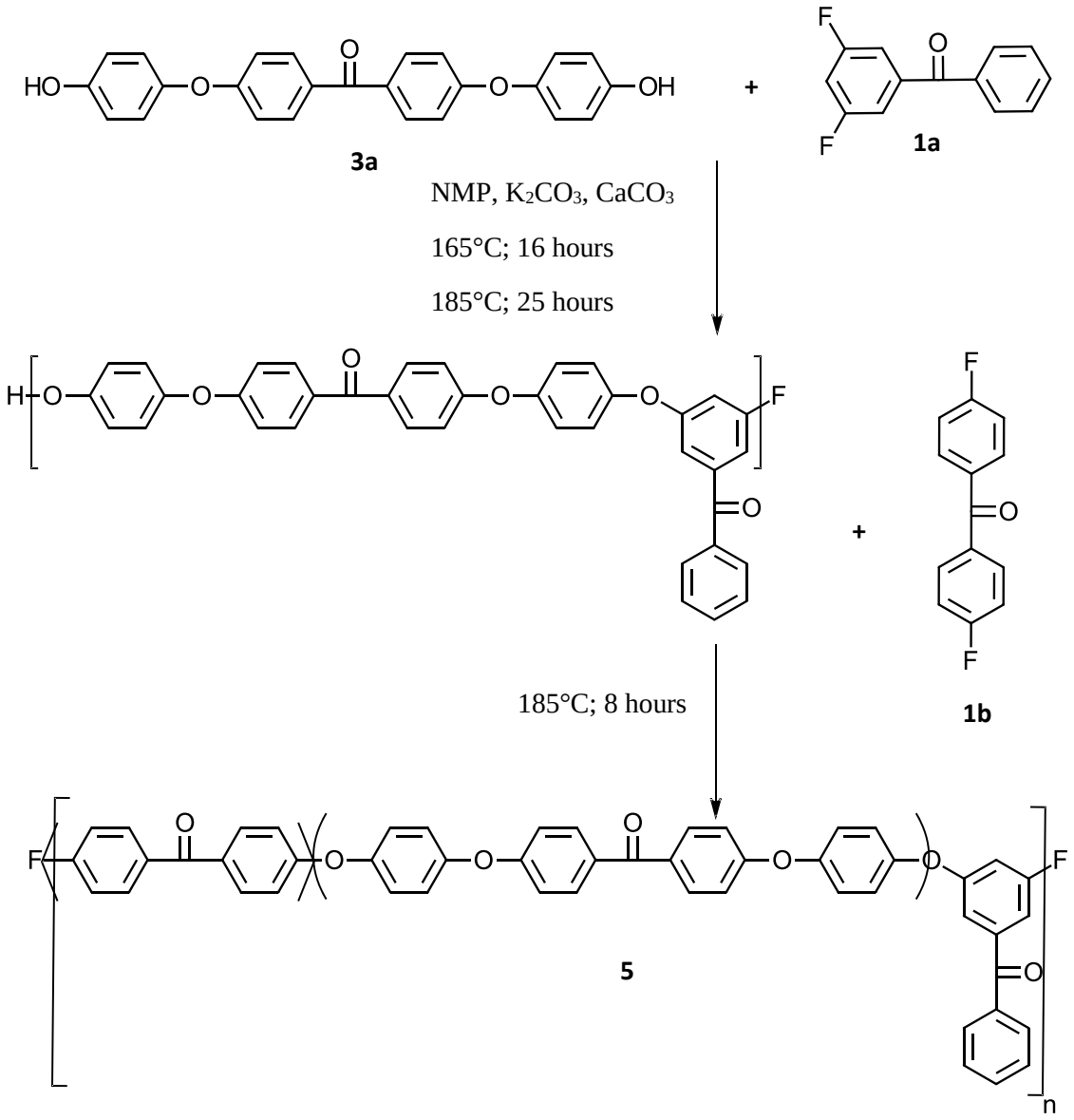
1.10 Current Project

Based on what has been previously done, it is the goal of this dissertation project to combine the method of RRCP with a benzophenone-based aryl trihalide, **2**, functionalized with several different nucleophiles; *p*-methoxyphenol, 4-bromophenol, 3-aminophenol, and *m*-cresol, **4a-4d**, affording products **6a-6d**, and which will result in a series of copolymers, **7a-7d**, that carry *p*-methoxyphenoxy, 4-bromophenoxy, 3-aminophenoxy, and *m*-tolyloxy units as functional groups, yet maintain some level of crystallinity (**Scheme 4**).



Scheme 4: Synthesis of Functionalized 75:25 PEEK-*co*-*meta*-PEEK, **7a-7d**

Before these functionalized copolymers can be made, however, 75:25 PEEK-*co-meta*-PEEK, **5**, will be synthesized to optimize reaction conditions and compare its structure with the desired functionalized copolymers via Differential Scanning Calorimetry (DSC). Using 3,5-difluorobenzophenone, **1a**, 4,4'-bis(4-hydroxyphenoxy) benzophenone, **3a**, abbreviated as "Big A_2", and 4,4'-difluorobenzophenone, **1b**, a NAS poly-condensation reaction was carried out in two steps, as shown in **Scheme 5**.



Scheme 5: Synthesis of 75:25 PEEK-*co*-*meta*-PEEK, **5**

EXPERIMENTAL

2.1 Instrumentation

All analyses of samples taken during the functionalization stage were done using a Gas Chromatography/Mass Spectrometer instrument, Hewlett-Packard (HP) 6890 Series GC with auto injection and a HP 5973 Mass Selective Detector/Quadrupole system. GC samples were prepared with a mixture of acetone and reaction solvent that was collected via glass pipette.

During the analysis of aliquots removed during poly-condensation, an AVANCE 300 MHz instrument, operating at either 300 or 75.5 MHz, was used to acquire ^{1}H and ^{13}C Nuclear Magnetic Resonance (NMR) spectra, respectively. NMR samples were prepared as a mixture 0.2 mL of the reaction solution and 0.4 mL of deuterated solvent, DMSO-d_6 or $CDCl_3$.

The melting points of the recrystallized solids were obtained using a MEL-TEMP instrument.

Differential Scanning Calorimetry and Thermogravimetric analysis were performed using TA Instruments, DSC Q200 and TGA Q500, at a heating rate of 10 °C/ min, under nitrogen gas or air.

2.2 Materials

All syntheses were performed under a nitrogen gas atmosphere. Potassium carbonate, K_2CO_3, was dried in an oven at 130°C before use. *N*-Methyl-2-pyrrolidone, NMP, was dried over and distilled from calcium hydride prior to use. 3,5-Difluorobenzophenone (3,5-DFK), **1a**, was synthesized via Friedel-Crafts acylation, while its 4,4'-

difluorobenzophenone isomer (4,4'-DFK), **1b**, was purchased from Sigma-Aldrich and recrystallized from hexanes. 4,4'-Bis[4-hydroxyphenoxy] benzophenone, **3a,** was synthesized using a method found in the literature.[53] 48% Hydrobromic acid in an aqueous solution was purchased from Sigma-Aldrich. Bisphenol A, **3b**, was used from a stock container and recrystallized from hexanes. The four nucleophiles used for functionalization, 4-methoxyphenol, 3-aminophenol, 4-bromophenol, and *m*-cresol (**4a-4d**), were purchased from Sigma-Aldrich and used as received. Benzene, fluorobenzene, and 3,5-difluorobenzoyl chloride were purchased from Oakwood Products and used as received.

2.3 Synthesis of 3,5-Difluorobenzophenone (3,5-DFK), **1a**

A 100 mL round bottomed (RB) flask, equipped with a stir bar, condenser, and nitrogen inlet was charged with 3,5-difluorobenzoyl chloride (5.00 mL, 42.5 mmol), benzene (45 mL, 829 mmol), and aluminum chloride (7.40 g, 55.5 mmol). The reaction mixture was stirred overnight followed by pouring into 300 mL of ice water containing several drops of concentrated HCl. The combined solution was transferred to a separatory funnel and 30-50 mL portions of chloroform were added twice. After the organic layer was separated, it was dried over magnesium sulfate and the solvents were removed via rotary evaporation resulting in yellowish-white crystals. The crystals were recrystallized from ethanol to afford 5.92 g (59.2% yield) of a white, cotton-like solid with a melting point range of 57-59 ºC. **^{13}C-DEPT90 NMR** (75.5 MHz, DMSO-d_6, δ): 107.8 (t), 112.6 (dd), 128.7 (s), 129.6 (s), 133.6 (s). **^{13}C-CPD NMR** (75.5 MHz DMSO-d_6, δ): 107.9 (t), 112.5 (dd), 128.7 (s), 129.3 (s), 133.3 (s), 135.7 (s), 140.4 (t), 160-163 (dd), 194.2 (t).[40]

2.4 Synthesis of 3,5,4'-Trifluorobenzophenone (TFK), 2

A 100 mL RB flask, equipped with a stir bar, condenser, and nitrogen inlet was charged with 3,5-difluorobenzoyl chloride (1.50 mL, 12.7 mmol) excess fluorobenzene (12.0 mL, 127.9 mmol), and aluminum chloride (2.05g, 15.4 mmol) and allowed to react for one day at room temperature under nitrogen gas. A calcium chloride drying tube was later added at the top of the condenser to keep the system dry. The solution was transferred to a beaker containing acidified water and then to a separatory funnel containing ethyl acetate. The organic solution was then separated and dried with magnesium sulfate. The solution was filtered, transferred to a RB flask and then evaporated via a rotary evaporator to afford a solid. The product was recrystallized several times with ethanol/water and then with isopropanol. The resulting product appeared as long, white crystals. Compared to a previous literature source having a melting point range of 65-67°C, the resulting melting temperature was revealed to be in a range of 63-65°C with a total yield of 1.79g (59.6%).[51]

^{1}H-NMR (300 MHz, $CDCl_3$, δ) 7.06 (tt; 1H), 7.21 (m; 2H), 7.29 (m; 2H), 7.85 (m; 2H). **^{13}C-CPD NMR** (75.5 MHz DMSO-d_6, δ): 107.6(t), 164.0-167.4 (d), 112.7(dd), 132.5 (d), 132.7 (d), 115.7 (d), 140.4 (t), 160.9-164.4 (dd), 192.4 (t).[51]

2.5 Synthesis of 4,4'-Bis[4-hydroxyphenoxy] benzophenone (Big A_2), 3a

A 100 mL RB flask containing a stir bar was charged with 4,4'-difluorobenzophenone (4.31g, 19.6 mmol), **1b**, *p*-methoxyphenol (7.61g, 61.3 mmol), potassium carbonate (12.3g, 89.0 mmol), and NMP (30 mL). The flask was connected to a condenser and the mixture was heated to 150ºC for 1 hour and then increased to 185ºC for

16 hours, according to a literature procedure derived from Hwang.[53] The resulting light-purple solution was poured into 500 mL of vigorously stirred water to afford a suspended, beige-colored solid, which was isolated via filtration. The resulting product, a protected version of **3a** that was verified via GC/MS [m/z=426], was dissolved in toluene (100 mL), transferred into a separatory funnel and washed with a saturated sodium carbonate solution (300 mL) resulting in three distinct layers: the organic layer, a salt emulsion, and the aqueous layer. The aqueous layer was vacuum filtered and the product reemerged. The color of the protected product was now white and it weighed out to be 7.31g (86.8% yield) NMR data was not possible due to the protected product being insoluble in deuterated chloroform and partially soluble in DMSO-d_6.

A 2 L RB flask, equipped with a reflux condenser and stir bar, was charged with an aqueous 48% hydrobromic acid solution (31 mL) and glacial acetic acid (375 mL) was added to the flask along with 7.31 g of protected Big A_2. The flask was immersed in an oil bath and heated to 130 ºC for 4 days. Monitoring via TLC was inconclusive, thus, after 5 days, a large excess of water to was poured into the solution to precipitate the product, which was then vacuum filtrated resulting in a white solid. The product was transferred to an Erlenmeyer flask containing ~300mL ethyl acetate, dissolved and then transferred to a 500 mL separatory funnel. The ethyl acetate solution was washed with an aqueous solution of 6g/500mL sodium bicarbonate. The ethyl acetate layer was then transferred to a beaker and magnesium sulfate was added to the solution and covered in a parafilm overnight. On the following day, the magnesium sulfate was removed via gravimetric filtration and the solvent was then removed via rotary evaporation to afford 4.09g (50.3% yield) of a white

colored solid. NMR spectra from product samples revealed that there were peaks for ethyl acetate and toluene. The product was placed into the drying pistol to remove traces of other solvents. After several attempts of recrystallization using ethanol, 3.96 g (50.3%) of the product was recovered with a melting temperature of 216-218°C, compared to a literature value of 214°C.[54] **^{13}C-DEPT90-NMR** (75.5 MHz DMSO-d_6, δ) 115.8, 116.4, 121.9, 131.9. **^{13}C-CPD NMR** (75.5 MHz DMSO-d_6, δ): 115.8, 116.4, 121.7, 131, 132, 146.5, 154.6, 162.1, 193.1.[50,53]

2.6 Synthesis of 75:25 PEEK-co-*meta*-PEEK, 5

3,5-Difluorobenzophenone (0.109g, 0.500 mmol), **1a**, potassium carbonate (0.209g, 1.51 mmol), calcium carbonate (0.154g, 1.54 mmol), Big A2 (0.400g, 1.00 mmol), **3a**, and NMP (1.80 mL) were added to a 10 mL RB flask containing a stir bar. The flask was then connected to a condenser under a nitrogen inlet and allowed to react at 165 ºC for 16 hours and raised to a temperature of 185 ºC for 25 hours. 4,4'-difluorobenzophenone (0.109g, 0.500 mmol), **1b**, was then added and reacted for 8 hours, according to a previous procedure.[50] The solution retained its low viscosity and was precipitated from acidified water and the product was isolated via vacuum filtration. After dissolving the entire product in 2 mL of hot NMP, 190 mL of isopropanol and a 10 mL water solution was prepared and used to precipitate the hot NMP solution, affording a 0.0692g amount of product. The product was dried after undergoing vacuum filtration and was examined using DSC for verification of the successful synthesis of 75:25PEEK-co-*meta*-PEEK, **5**.

2.7 Synthesis of Mono-substituted TFK with varying functional groups

All reactions were performed using similar reaction conditions numerous times. The amount of aryl trihalide monomer, slight excess nucleophile, base, and polar aprotic solvent were relatively constant throughout each type of functionalization.[51]

2.7.1 Mono-substitution of TFK with 4-methoxyphenol, 6a

A 5 mL RBF containing a stir bar was charged with *p*-methoxyphenol (0.0666 g, 0.536 mmol), TFK (0.119 g, 0.504 mmol), K_2CO_3 (0.107g, 0.774 mmol), and 0.800 mL NMP. The reaction flask was connected to a condenser with a N_2 gas inlet, lowered into a mineral oil bath and heated at 110°C for 4 days. Analysis of an aliquot via GC/MS indicated complete conversion to the desired mono-substituted product.

2.7.2 Mono-substitution of TFK with 3-aminophenol, 6b

To a 5 mL RBF, equipped with reflux condenser and a stir bar, were added TFK (0.120g, 0.451 mmol), *m*-cresol (0.0624 g, 0.572 mmol), potassium carbonate (0.112 g, 0.810 mmol), and NMP (0.800 mL) and heated at a temperature of 110°C. A GC/MS sample performed after three days showed unreacted TFK present at 0.9% and the following day was reduced to 0.23%.

2.7.3 Mono-substitution of TFK with 4-bromophenol, 6c

A 5mL RBF containing a stir bar was charged with TFK (0.118g, 0.500 mmol), 4-Bromophenol (0.0906g, 0.524 mmol), potassium carbonate (0.112g, 0.810 mmol), and NMP (0.800 mL) and equipped with a reflux condenser under nitrogen gas. The flask was immersed and heated in a mineral-oil bath at a temperature of 110°C. After four days of

heating, a GC/MS sample was taken and revealed the presence of mono-substituted TFK with 4-Bromophenol [98.3%]. No unreacted TFK peak was present.

2.7.4 Mono-substitution of TFK with m-cresol, 6d

To a 5mL RBF, TFK (0.117g, 0.495 mmol), *m-cresol* (0.0615g 0,569 mmol) 0.109g K_2CO_3 (0.109g, 0.789 mmol), and NMP (0.850 mL) were added and equipped with a reflux condenser and a N_2 gas inlet was attached at the top. The reaction was heated at 110°C and the flask was immersed into a mineral-oil bath for 4 days. After four days of heating, a GC/MS analysis confirmed the presence of mono-substituted TFK [89.4%], di-substituted [10.3%], and an isomer of mono-substitution [0.324%]. No TFK was present.

2.8 Synthesis of Functionalized 75:25 PEEK-co-*meta*-PEEK, 7a-7d

Verification of mono-substituted product with negligible, unreacted TFK was crucial for each functionalization to continue toward the second step of the reaction: introduction of Big A2, extra potassium carbonate, extra NMP, and an elevated temperature to the system in order to displace the fluorine atoms meta to the carbonyl group on TFK.

2.8.1 Functionalization with 4-methoxyphenol, 7a

Subsequently, Big A_2 (0.401 g, 1.01 mmol) was added to the system containing mono-substituted TFK with 4-methoxyphenol, along with K_2CO_3 (0.421 g, 3.05 mmol) and NMP (1.00 mL). The reaction was heated at 185°C for 16 hours, at which point 4,4'-DFK (0.0855g, 0.392 mmol), was added. After one hour, the reaction began to harden and extra amounts of NMP (2 mL portions) did not allow the solution to lower in its viscosity.

2.8.2 Functionalization with 3-aminophenol, 7b

To the reaction flask containing mono-substituted TFK with 3-aminophenol, Big A_2 (0.405g, 1.02 mmol), K_2CO_3 (0.428g, 3.10 mmol), and NMP (1.00 mL) were added and allowed to react for 18 hours at 185°C. 4,4'-DFK (0.110g, 0.500 mmol) was added and allowed to react for a further 8 hours at 150°C. The solution somewhat solidified but dissolved when 4 mL of NMP was added. The resulting solution was poured into a beaker containing 1000 mL of water containing drops of hydrochloric acid to afford a light-tan colored polymer. 0.040g of the polymer sample was dissolved into a 0.300 mL solution of NMP and was successfully re-precipitated with 100 mL water. The rest of the polymer was dissolved in 2 mL of NMP but re-precipitation was unsuccessful.

2.8.3 Functionalization with 4-bromophenol, 7c

To the reaction flask containing mono-substituted TFK with 4-bromophenol, Big A_2 (0.401g, 1.00 mmol), potassium carbonate (0.430g, 3.11 mmol), and NMP (1.00 mL) were added and allowed to react at 185°C for 16 hours. 4,4'-DFK (0.109g, 0.500 mmol) was added to the system and allowed to react at 150°C. The reaction gelled after nearly an hour of heating and the reaction was stopped.

2.8.4 Functionalization with m-cresol, 7d

To the reaction flask containing mono-substituted TFK with m-cresol, Big A_2 (0.339g, 1.00 mmol), 0.461g K_2CO_3 (0.461g, 3.01 mmol), and NMP (1.00 mL) were added and reacted at a temperature of 185°C for 17 hours. The solution from the flask appeared to be dark brown colored and was pipetted to a 25-mL round-bottomed flask along with NMP (4 mL) and 4,4'-DFK (0.110g, 0.500 mmol) was added to the flask and reacted at 150°C for 6 hours. The reaction was stopped and, while still hot, was pipetted to a 250 mL

solution of acidified water. A light-tan solid was precipitated and vacuum filtrated. Solubility tests with six solvents were performed and resulted in the product being partially soluble in NMP, THF, DMSO, and chloroform. The product was only soluble in NMP and chloroform when heated to their boiling points.

2.9 Synthesis of Mono-substituted TFK with Big A_2, 3a, and Bisphenol A, 3b, at various reaction times

Numerous unsuccessful attempts at synthesizing functionalized 75:25 PEEK-co-*meta*-PEEK resulted in examining the displacement of the 3,5-meta-fluorines during various times of the reaction by using two different nucleophiles: Big A_2, **3a,** and Bisphenol A, **3b**.

2.9.1. Mono-substituted TFK reacting with Big A_2, 3a

TFK (0.118g, 0.500 mmol), K_2CO_3 (0.119g, 0.861 mmol), *p*-methoxyphenol (0.0684g, 0.551 mmol), $CaCO_3$ (0.0841g, 0.840 mmol), and NMP (0.800 mL) were added to a 5-mL round-bottomed flask and equipped with a stir bar and a reflux condenser under nitrogen gas. The flask was heated at 110°C for 4 days in a mineral oil bath. GC/MS analysis revealed 97.1% mono-substitution, 2.86% di-substitution, and 0.015% unreacted TFK present. A sample, 0.200 mL, was removed for NMR analysis. Big A_2 (0.299g, 0.750 mmol), K_2CO_3 (0.311g, 2.25 mmol) and NMP (0.75 mL) were then added to the flask at an elevated temperature of 185°. Samples at different reaction times were taken and analyzed via nuclear magnetic resonance spectroscopy.

2.9.2. Mono-substituted TFK reacting with Bisphenol A, 3b

TFK (0.302g, 1.27 mmol), K_2CO_3 (0.282g, 2.04 mmol), *p*-methoxphenol (0.161g, 1.30 mmol), and NMP (2.00 mmol) were added to a 5 ml RB flask, equipped with a stir bar and a reflux condenser under nitrogen gas. The flask was immersed and heated in a

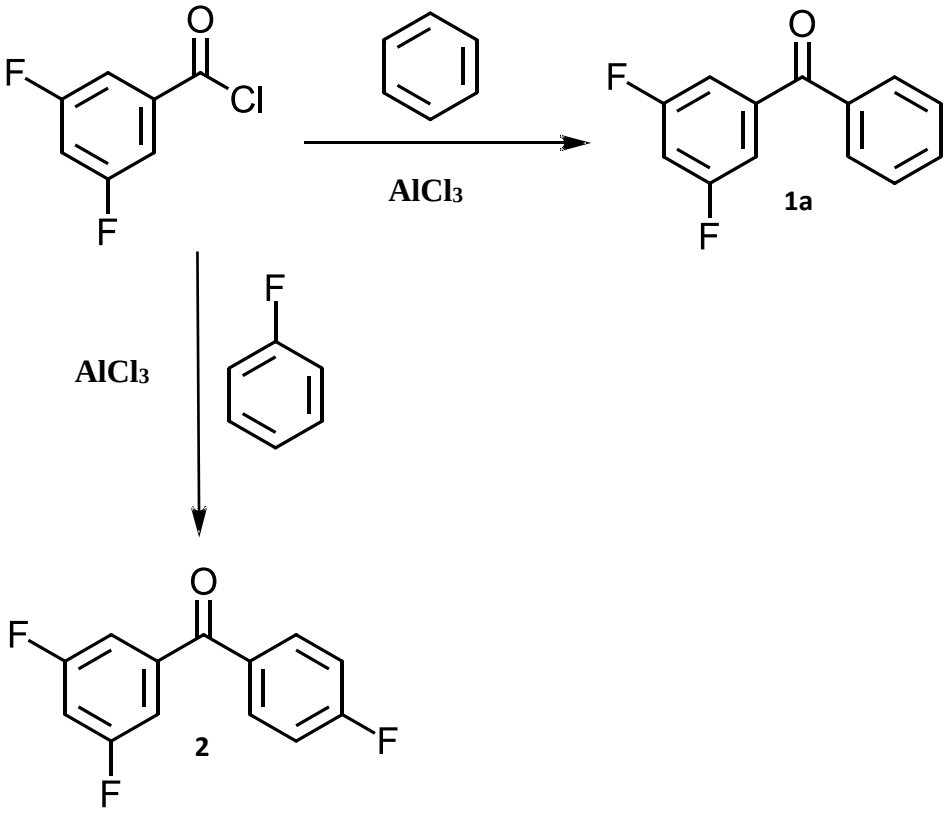
mineral-oil bath at a temperature of 110°C. After four days of heating and adding extra *p*-methoxyphenol (0.0033g, 0.0266 mmol), a GC/MS sample revealed the presence of negligible TFK [0.029%], mono-substituted TFK [97.582%], and di-substituted TFK [2.389%]. Bisphenol A, **3b** (0.580g, 2.54 mmol), and potassium carbonate (1.06g, 7.67 mmol) were added to the flask and allowed to react at an elevated temperature of 185°C. NMR samples were pipetted from the flask at 4 hours, 11 hours, 19 hours, and 32 hours of reaction and compared to monitor the displacement of meta-fluorine groups on TFK.

RESULTS AND DISCUSSION

The main goal of the research project was to synthesize functionalized 75:25 PEEK-*co*-*meta*-PEEK systems using a reactivity ratio controlled poly-condensation (RRCP) approach. A secondary goal emerged that involved examining the *meta*-fluorine displacement of functionalized TFK, with Big A_2 and Bisphenol A. The secondary goal allowed the determination of the optimal reaction time needed to ensure complete incorporation of the 3,5-derivative prior to addition of the traditional PEEK monomer, 4,4'-difluorobenzophenone, **1b**. A successful displacement of the fluorine atoms at an optimal reaction time would allow the reaction to avoid gelling and retain its low viscosity during heating and the precipitation of the solution.

Two fluorinated monomers, 3,5-difluorobenzophenone, **1a**, and 4',3,5-trifluorobenzophenone, **2**, were synthesized via Friedel Crafts acylation. The former was needed to react with 4,4'-Bis[4-hydroxyphenoxy] benzophenone, **3a,** for the synthesis of functionalized 75:25 PEEK-*co*-*meta*-PEEK, **5**, while the latter was needed to serve as a site

of functionalization in which selected functional groups can displace a fluorine atom *para* to the electron-withdrawing group.



Scheme 6: Synthesis of Di and Trifluoronated Ketone, **1a** and **2**, via Friedel Crafts Acylation

During Friedel Crafts acylation, 3,5-difluorobenzoyl chloride and benzene were the main precursors to synthesize **1a**, but fluorobenzene was used to introduce a third fluorinated carbon for the production of **2,** as shown in **Scheme 6**. The *para*-fluorine atom on **2** is a site of reaction that can be displaced at low temperatures between 110°C-120°C with functional groups that act as nucleophiles (**4a-4d**) located on its lower benzene ring.

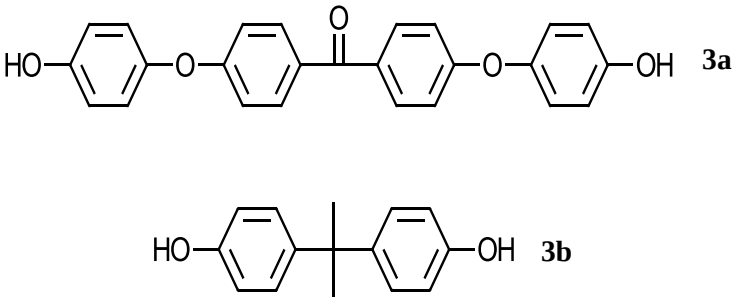


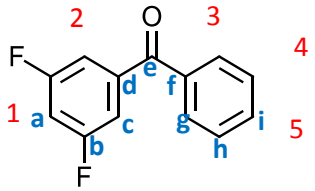
Figure 6: Structure of 4,4'-Bis[4-hydroxyphenoxy] benzophenone, **3a,** and Bisphenol A, **3b**

Both monomers require a bisphenol to synthesize PEEK-like compounds during polymerization. Bisphenols, such as, **3a**, and, **3b**, form the polymeric backbone at the upper ring containing the two fluorine atoms *meta* to the carbonyl group at sufficient high temperatures, such as those reaching ~185°C (**Figure 6**). Once the monomer's *meta*-fluorine atoms were displaced, the length of the chain is controlled with additional **3a** and 4,4'-difluorobenzophenone, **1b**. The differences in length of the polymer influence its chemical properties, such as crystallinity and glass transition temperatures.

3.1 Synthesis of 3,5-Difluorobenzophenone (DFK), 1a

Replicating Fortney's PEEK-co-meta-PEEK copolymer required the synthesis of 3,5-difluorobenzophenone, **1a**. Reaction of 3,5-difluorobenzoyl chloride, with benzene for 24 hours, in the presence of aluminum chloride afforded, after workup and recrystallization with ethanol, white, spike-shaped crystals. ^{13}C-DEPT90 and CPD spectra were obtained that showed five unique carbon peaks for the former and nine unique carbon atoms for the latter as shown in **Figure 7**. Carbon 1 had a chemical shift of 107.8ppm as a triplet due to coupling between two fluorine atoms. Carbon 2 was revealed to be a doublet of doublets

with a chemical shift of 112.6 ppm. Unlike carbon 1, carbon 2 was coupled by two fluorine atoms that were non-equivalent at that position. Carbons 4, 5, and 3 appeared as singlets with shifts at 128.7, 129.6, and 133.6ppm, respectively. The CPD NMR spectra showed carbons a, d, and e having triplets at 107.9, 140.4 and 194.2 ppm as a result of coupling with two equivalent fluorine atoms. Carbons c and b were revealed to be doublet of doublets with a shift of 112.5 and 160-163 ppm, respectively. Carbons h, i, g, and f appeared as singlets at 128.7, 129.3, 133.3, and 135.7ppm.



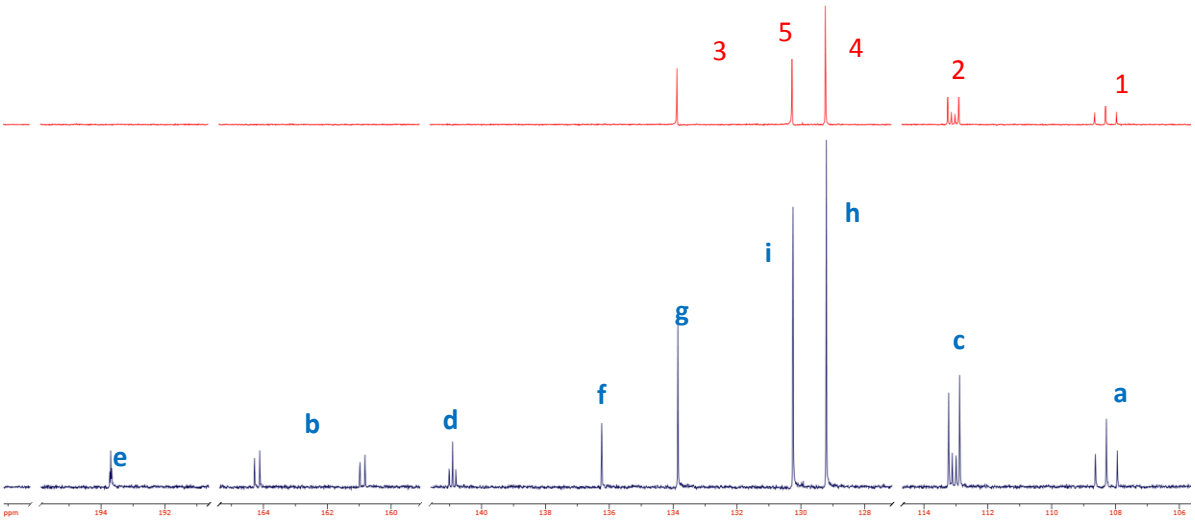


Figure 7: Overlay of 75.5 MHz ^{13}C-DEPT-90 [top] and ^{13}C-CPD [bottom] NMR (DMSO-d_6) spectra of **1a**

3.2 Synthesis of 3,5,4'-Trifluorobenzophenone (TFK), 2

The process of synthesizing TFK, **2**, used 3,5-benzoylchloride with fluorobenzene in the presence of aluminum chloride. The crude product was recrystallized with an ethanol/water solution and later with isopropanol that afforded a white-colored solid. The structure was confirmed via its ^{1}H and ^{13}C NMR spectra. In **Figure 8**, the proton NMR spectrum revealed four unique peaks, one of which was proton **a**, a triplet of triplets, at 7.06ppm resulting from two fluorine atoms coupling to the proton between them. Protons **d**, **b**, and **c** were revealed to be multiplets with chemical shifts of 7.21, 7.29, and 7.85ppm, respectively. The CPD ^{13}C NMR spectrum in **Figure 9** revealed nine unique peaks, with carbon **a,** carbon **d**, and carbon **e** appearing as triplets at 107.9 ppm, 140.4 ppm, and 192 ppm, respectively, which were coupled to the fluorine atoms located in the upper ring of the compound. Carbons **b** and **c** appear as doublets of doublets as a result of coupling with two non-equivalent fluorine atoms, (112.7 ppm and 160.9-164.4 ppm, respectively). The carbons that appear as doublets as a result of coupling with the ortho-fluorine atom on the lower ring are **f**, **g**, **h**, and **i**, at chemical shifts of 132.5, 132.7, 115.7, and 164.0-167.4 ppm, respectively.

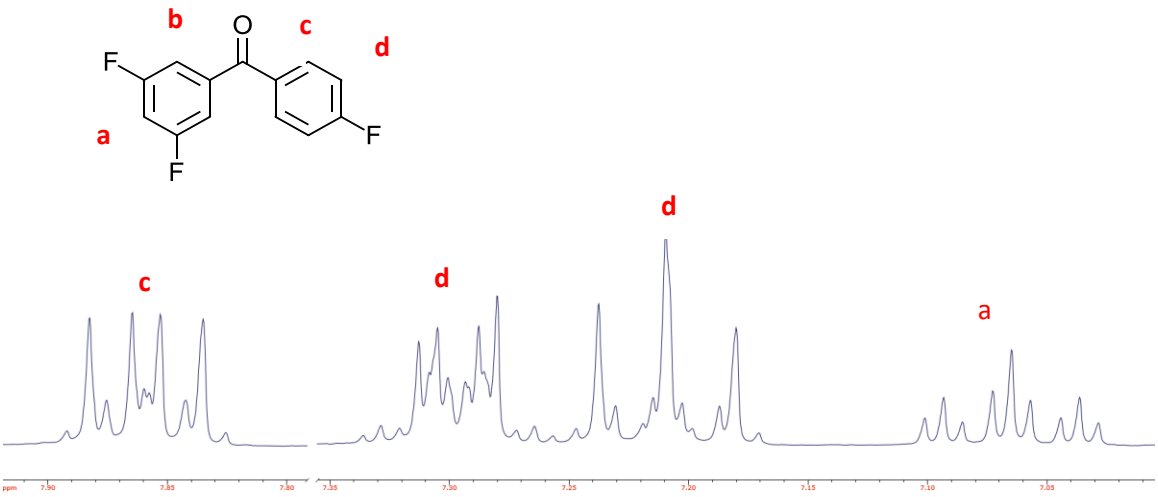


Figure 8: 300 MHz ^{1}H-NMR ($CDCl_3$) spectrum of 3,5,4'-trifluorobenzophenone (TFK), **2**

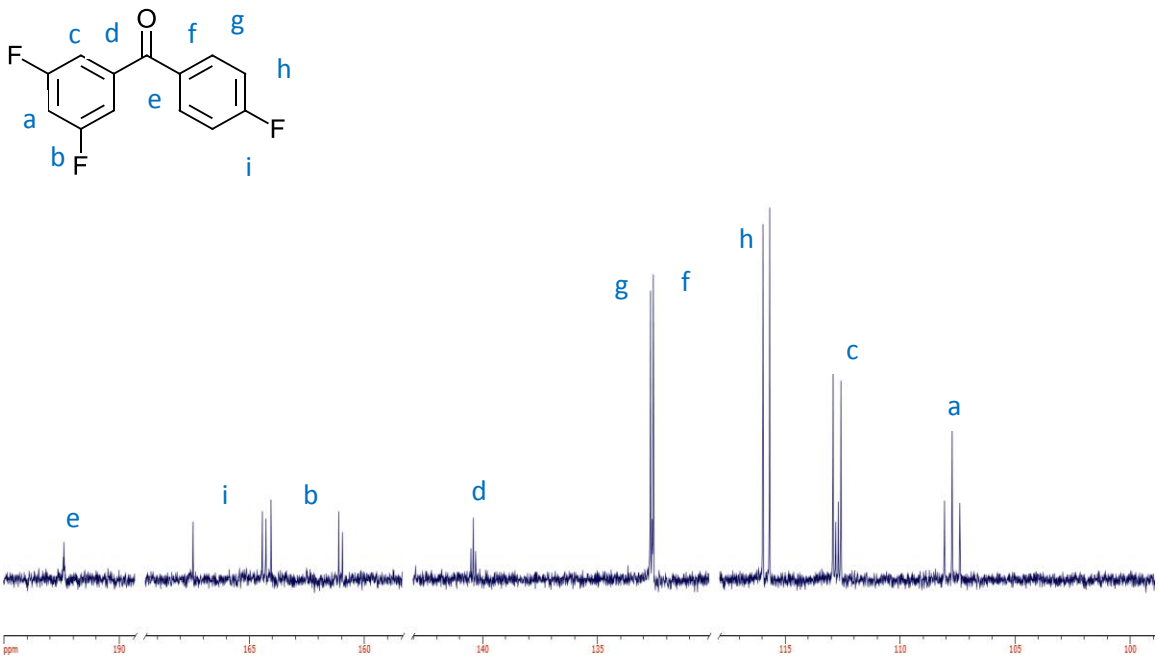
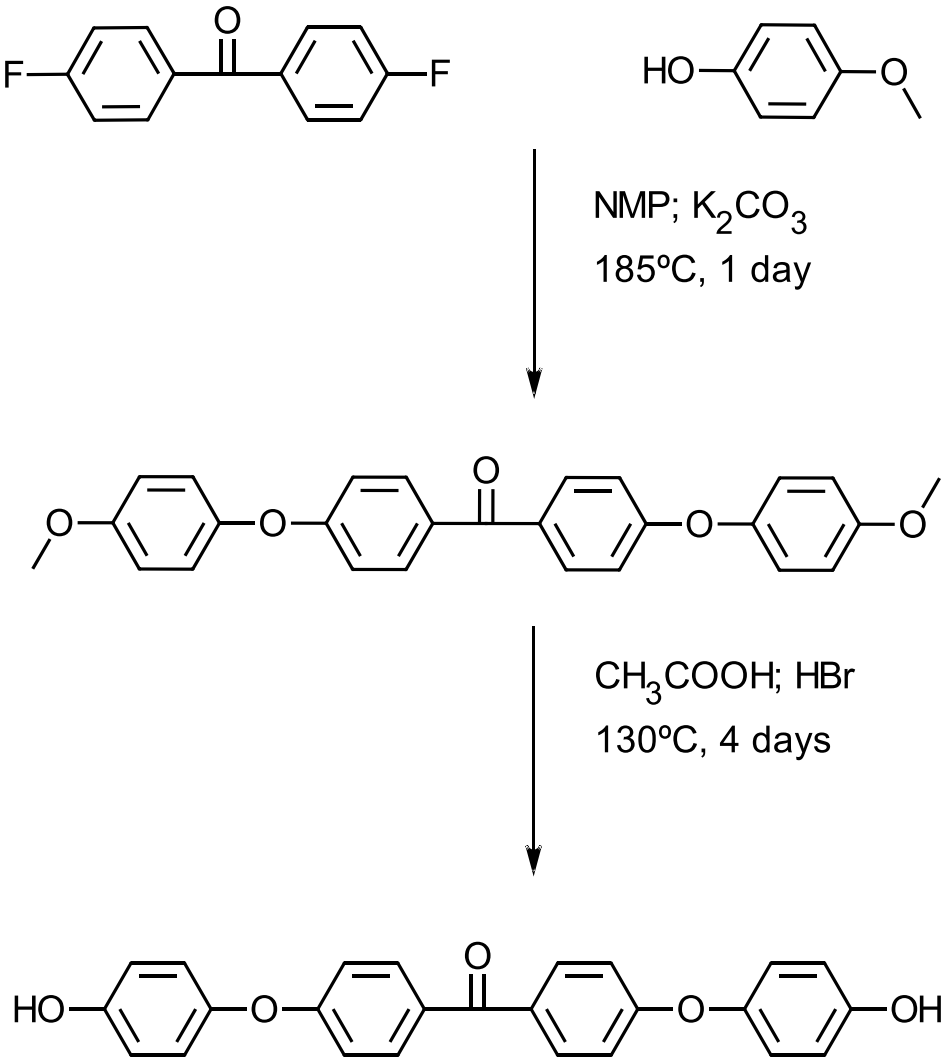


Figure 9: 75.5 MHz ^{13}C-CPD NMR ($CDCl_3$) spectrum of 3,5,4'-trifluorobenzophenone (TFK), **2**

3.3 Synthesis of 4,4'-Bis[4-hydroxyphenoxy] benzophenone, 3a



Scheme 7: De-protection of 4,4'-Bis[4-methoxyphenoxy] benzophenone

As shown in **Scheme 7**, a linear difluorinated compound, **1b**, reacted with *p*-methoxyphenol to yield an intermediate of **3a**, which was deprotected in the presence of hydrobromic acid and glacial acetic acid to afford 7.31g (86.8%) of product. The molecule was needed to provide a "PEEK"-like characteristic to replicate one of Fortney's polymers.

The structure of **3a** was confirmed via ^{13}C-CPD and ^{13}C-DEPT-90 NMR analysis and the spectra can be seen in **Figure 10**.

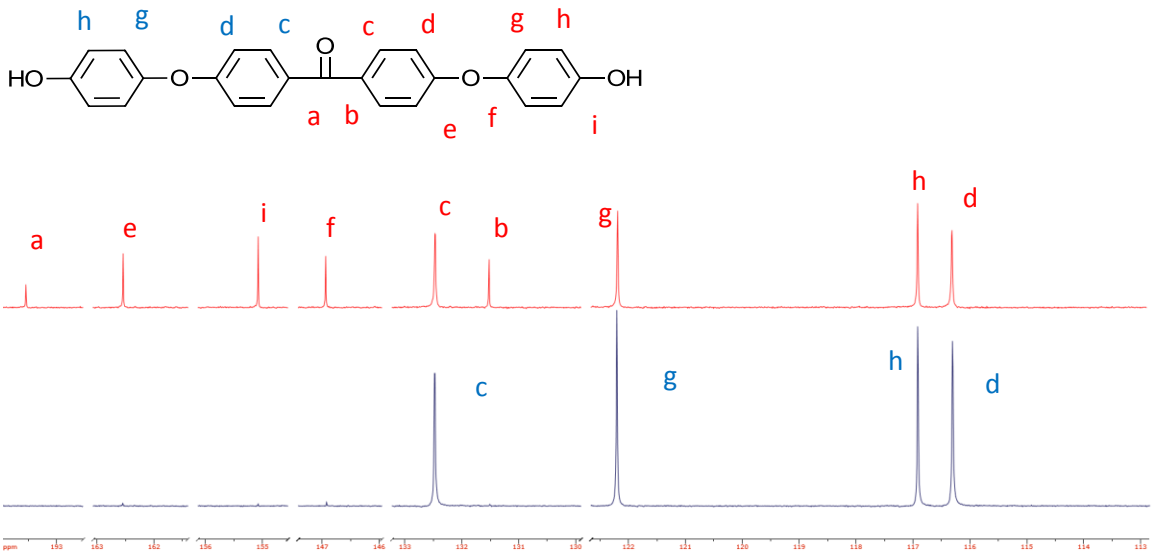


Figure 10: Overlay of 75.5 MHz ^{13}C-CPD [red] and ^{13}C-DEPT90 [blue] NMR spectrum in a solution of DMSO-*d6* of Big A2, **3a**.

Nine unique carbons from the ^{13}C-CPD NMR spectrum and four unique carbons from the ^{13}C DEPT90 confirmed the presence of Big A_2. Carbon a was observed at 193.1ppm, as a singlet. Carbons c, d, g, and h were singlets with a chemical shift of 132.0, 115.8, 121.7, and 116.4ppm, respectively. Quaternary carbons such as b, e, f, and i appeared as singlets measured to be 131.0, 162.1, 146.5, and 154.6, respectively. In comparison to the DEPT90 spectrum, carbons d, h, g, and c were observed as singlets at 115.8, 116.4, 121.9, and 131.9 ppm, respectively.

3.4 Synthesis and Differential Scanning Calorimetry analysis of 75:25 PEEK-*co-meta*-PEEK, 5

The synthesis of 75:25 PEEK-*co-meta*-PEEK, **5**, was achieved as outlined in **Scheme 5**. Reaction of 3,5-difluorobenzophenone, **2**, and Big A_2, **3a**, for 16 hours at 165°C and 25 hours at 185°C was followed by the addition of 4,4'-DFK, **1b**, with subsequent heating at the same temperature for 8 hours. Numerous attempts at synthesizing the polymer were done until a mixture of bases that contained calcium carbonate/potassium carbonate was added to the reaction and retained its low viscosity after 4,4'-DFK, **1b**, was incorporated into the system. After reprecipitation in acidified water and isopropanol/water, a beige-colored, granular-like solid was isolated in low yield 0.0629 g (1.04%).

A sample of the solid was analyzed via differential scanning calorimetry (DSC) and the traces are shown in **Figure 11**. Two endothermic and one exothermic transition were observed. The T_g, T_c, and T_m were observed to be ~140°C, ~200°C, and ~285°C. The presence of a T_m indicated that the sample made to replicate Fortney's polymer was semi-crystalline. The degradation temperature at 5% weight loss ($T_{d5\%}$) was determined, via TGA, to be 542°C, which was different in contrast to Fortney's previous value of 508°C. From Fortney's project, T_g was determined to be 137°C but T_c, and T_m were not given but are estimated to be 230°C and 275°C, respectively. Fortney verified the presence of semi-crystalline polymers via X-Ray diffraction, despite not being observed in DSC traces.[50]

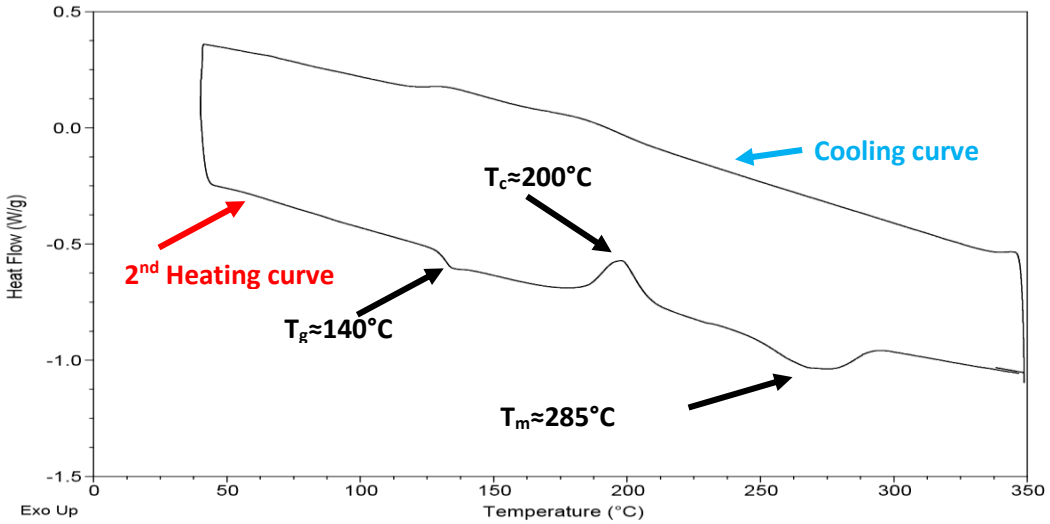
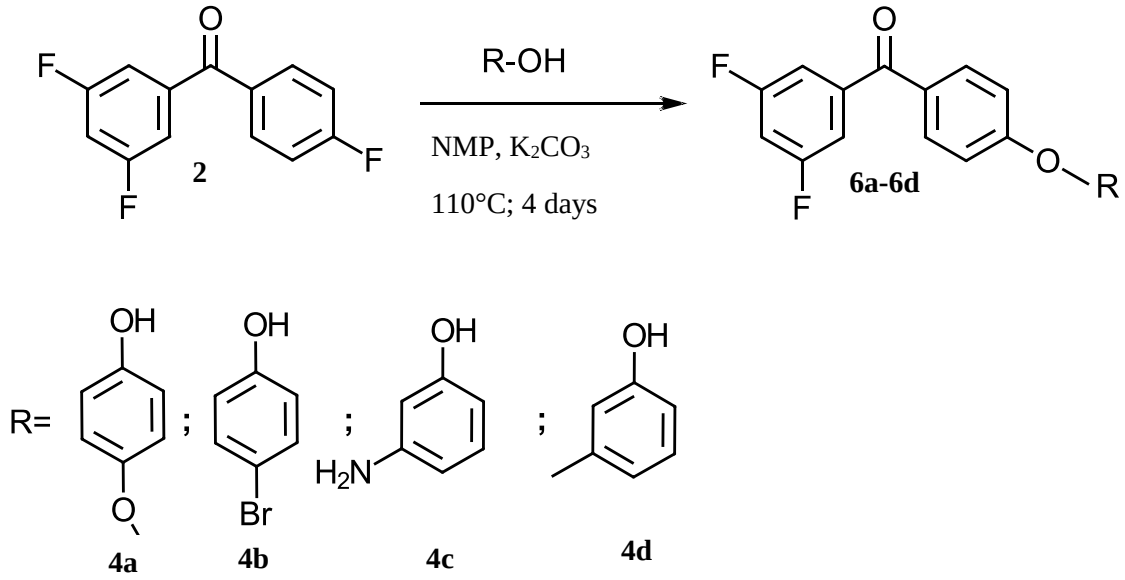


Figure 11: DSC trace of 75:25PEEK-co-*meta*-PEEK (a) Cooling curve and (b) 2nd Heating curve

3.5 Synthesis of Mono-substituted TFK with various functional groups (6a-6d) and the poly-condensation of mono-substituted TFK with Big A_2 and 4,4'-DFK, 1a

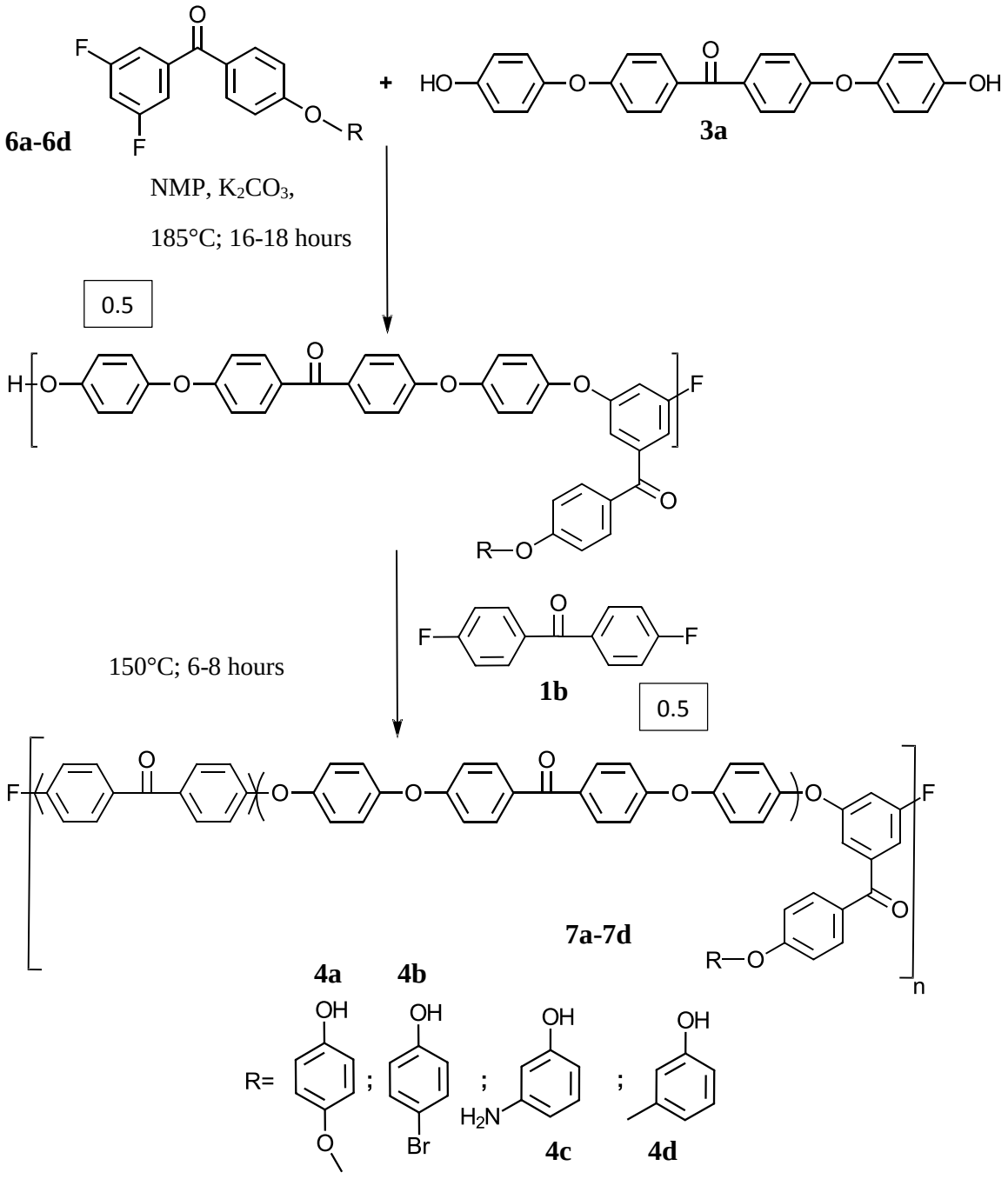


Scheme 8: Mono-substitution of 3,5,4'-trifluorobenzophenone (TFK), **2**, with varying functional groups, **4a-4d**

The preparation of functionalized 75:25 PEEK-co-*meta*-PEEK requires that monomer **2** undergo NAS reactions, displacing only its *para*-positioned fluorine atom at a low temperature of 110-120°C. Four different types of nucleophiles; *p*-methoxyphenol, 4-bromophenol, 3-aminophenol, and *m*-cresol, were used to afford the corresponding functionalized TFK monomers, as shown in **Scheme 8**. This is an example of pre-functionalization, in which the functional group is introduced to a monomer before being incorporated into the polymeric chain. All mono-substitutions were confirmed via GC/MS analysis with m/z values of 340.32, 389.19, 325.31, 324.32 for **6a**, **6b**, **6c**, and **6d**, respectively. In each reaction, the amount of mono-substituted product reached conversions of 98%, while unreacted TFK was revealed to be present in amounts less than one percent. The small amount of TFK was a result of adding excess phenol to the reaction,

despite causing an increase in the amount of di-substituted product. As an expected side effect, some samples have an amount of di-substituted TFK that was revealed to be >1%. While not affecting the reaction with the problem of cross-linking, the presence of di-substituted TFK may result in low molecular yields for the end product polymer.

Each mono-substituted TFK, **6a-6d**, would now be ready for the next step of the reaction: undergoing poly-condensation with Big A_2, **3a**, at an elevated temperature of 185°C for 16-18 hours (**Scheme 9**). 4,4'-DFK, **1b**, was added to the mixture and allowed to react for 6-8 hours at a temperature of 150°C to synthesize the desired polymers, **7a-7d**. Polymers **7a** and **7b** were not successfully precipitated as a result of gelling, while **7c** and **7d** afforded products after successfully precipitating the solution from isopropanol-water.



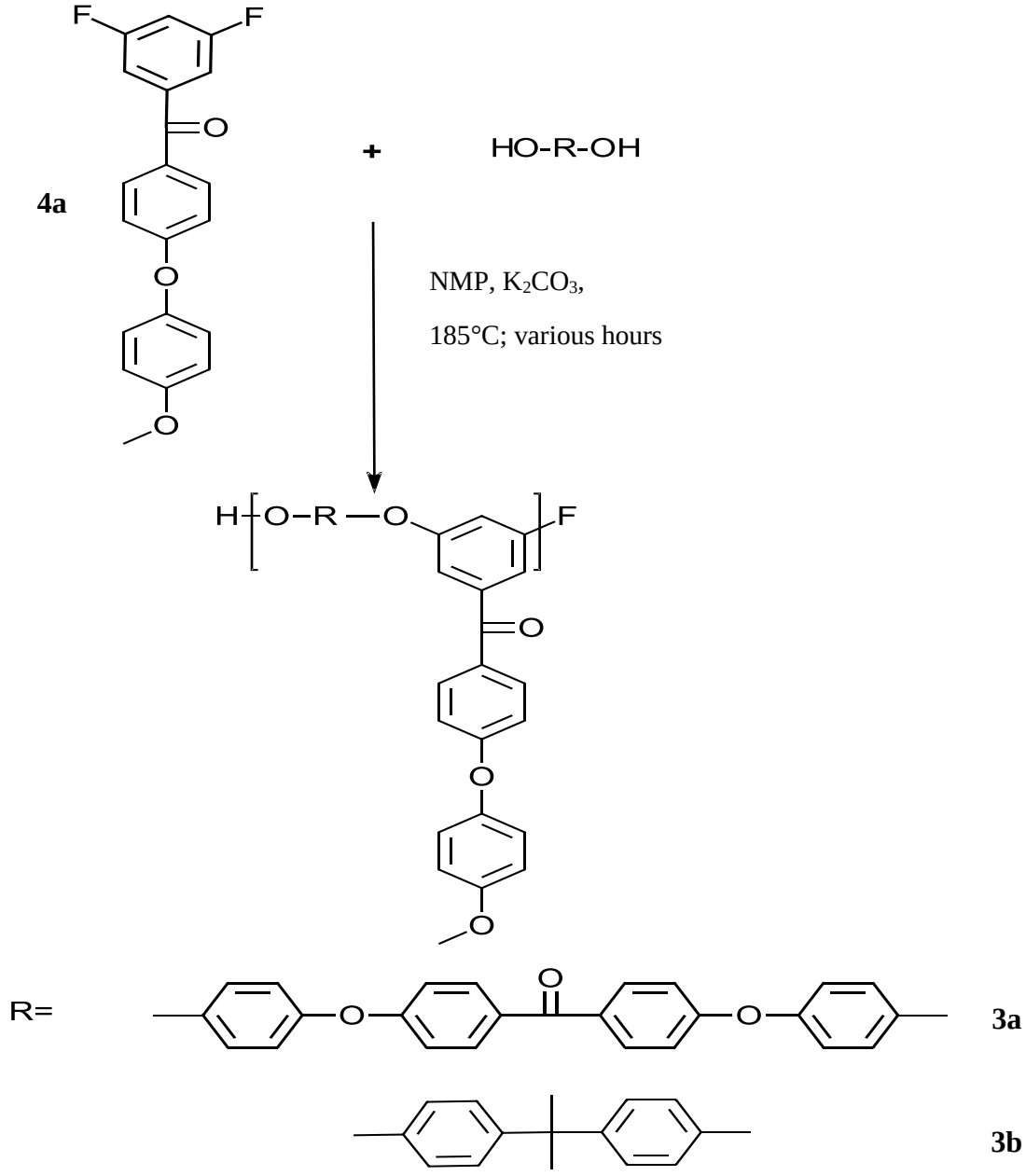
Scheme 9: Poly-condensation of Mono-Substituted TFK, **6a-6d**, with Big A_2, **3a**, and 4,4'-difluorobenzophenone**, 1b**

Solubility tests were performed on **7d**, but not on **7c** due to difficulties with precipitating the polymer. **Table 1** shows the results of those tests; the polymer was partially soluble in NMP, THF, DMSO, and chloroform at room temperature, but remained insoluble with toluene. When the solvent was heated to its boiling point, it completely dissolved in NMP and chloroform but remained partially soluble in THF and DMSO-d_6.

	Room Temperature	**Boiling Point**
NMP	**+/-**	**+**
THF	**+/-**	**+/-**
DMSO	**+/-**	**+/-**
Chloroform	**+/-**	**+**
Toluene	**-**	**-**

Table 1: Solubility Tests of **7d** with various solvents (**+/-**; partially soluble, +; soluble, -; insoluble)

3.6 Meta-Fluorine Displacement of Functionalized TFK with Big A_2 and Bisphenol A at various times



Scheme 10: Condensation of TFK-functionalized *p*-methoxyphenol, **6a**, with Big A_2, **3a**, and bisphenol A, **3b**

Given the difficulties in preparing soluble, functionalized 75:25 PEEK-co-*meta*-PEEK, it was decided to take a deeper look into the displacement reactions of mono-substituted TFK systems. Two separate nucleophiles, Big A_2 **(3a),** and bisphenol A (**3b**), in the presence of potassium carbonate and NMP at a temperature of 185°C, as shown in **Scheme 10**, were explored. The mono-substituted TFK was prepared using *p*-methoxyphenol as the nucleophile. The reaction was monitored by removing aliquots, at selected reaction times, which were then analyzed using ^{13}C NMR spectroscopy.

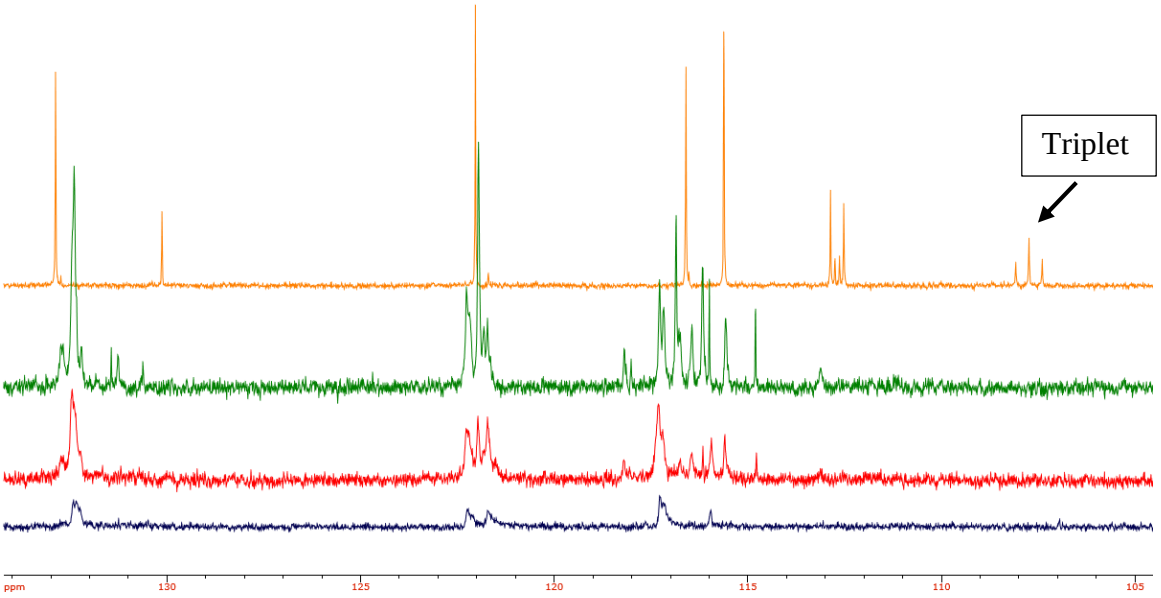


Figure 12: Overlay of 75.5 MHz ^{13}C-CPD NMR spectrum (DMSO-*d6*) of the reaction of TFK functionalized with *p*-methoxyphenol and Big A_2 at 0 hours (Before the addition of Big A_2), 8 hours, 16 hours, and 55 hours.

In **Figure 12**, 0.2 mL samples of the reaction solutions were taken at different times and compared with each other and to a sample before **3b** was added to the system, highlighted in orange. The spectrum at 0 hours revealed a triplet at 107.2 ppm due to coupling between two fluorine atoms. It is expected to view a triplet before any nucleophile begins to displace the fluorine atoms on the aryl halide. After **3b** was added to the reaction, the triplet disappeared after the reaction ran for 8 hours, highlighted in green, but it could not be verified if a doublet or a singlet remained due to overlapping of multiple singlets and peak broadening. A lack of a triplet indicated that a fluorine atom, if not both, were being successfully displaced. Spectra at 16 hours (red) and 55 hours (indigo) revealed a decrease in the number of peaks present and constant peak broadening, making difficult to pick out any other peaks that are hidden. Previous sampling after filtering did not yield

readable spectra, since they were barely any peaks visible to label, with the exception of the deuterated solvent and reaction solvent.

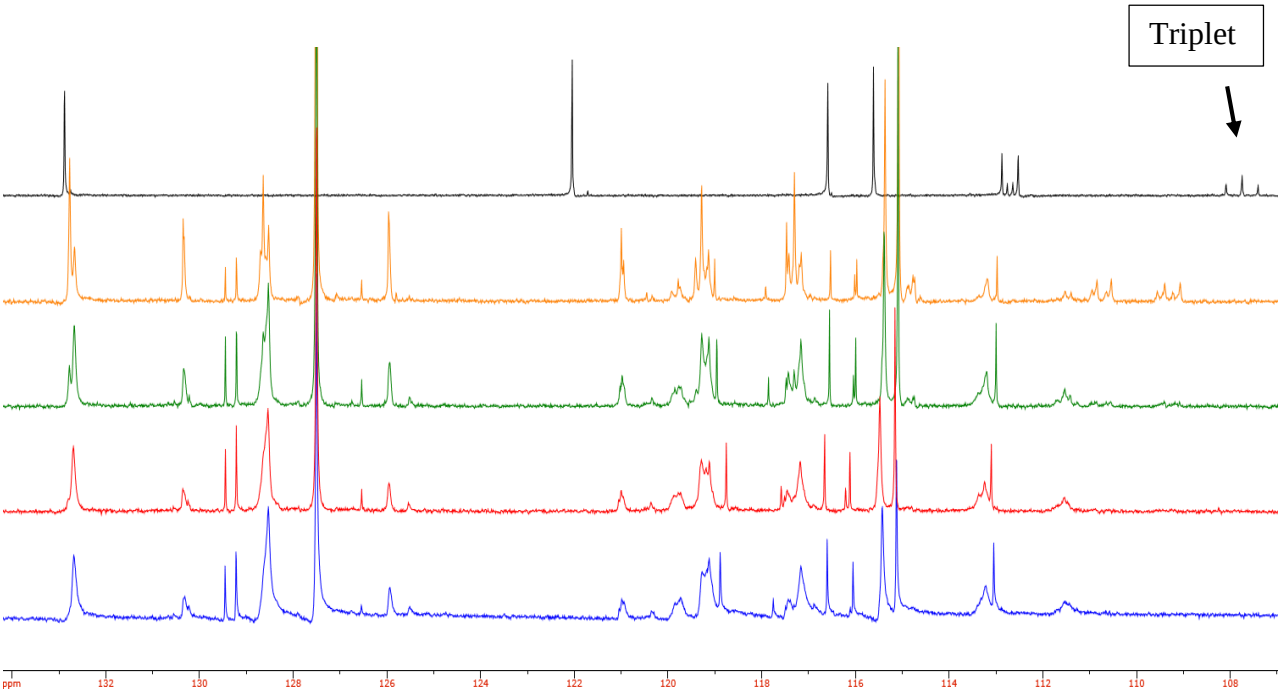


Figure 13: Overlay of 75.5 MHz ^{13}C-DEPT90 NMR spectrum (DMSO-*d6*) of TFK functionalized with *p*-methoxyphenol and Bisphenol A, 4 hours, 11 hours, 19 hours, and 32 hours, compared to mono-substituted TFK before the addition of Bisphenol A (0 hours).

Using Bisphenol A, **3b**, as a nucleophile, TFK functionalized with *p*-methoxyphenol was examined at five different reaction times to acquire the ^{13}C-DEPT90 NMR spectra seen in **Figure 13**. Before Bisphenol A was added, a spectrum of mono-substituted TFK at 0 hours showed a triplet at 107.2 ppm caused by coupling of the *meta*-fluorine atoms, which is expected before it reduces to a singlet after the nucleophile is added to the reaction and displaces the halides. 4 hours (orange) into the reaction revealed a spectrum with various peaks, some of which were singlets and others that were multiplets. No triplet was found to indicate a coupled carbon, which indicated that at least one of the

fluorine atoms were being displaced. Spectra at 11 hours (green) and 19 hours (red) showed a slight decrease in the number of peaks and other peaks decreased in split number, that is, doublets were becoming broad enough to become singlets. At 32 hours (indigo), most of the peaks were revealed to be broad singlets.

Comparing similar NMR data obtained from Fortney and Boakye, it was revealed from **Figures 12** and **13** that displacement one fluorine atom occurs when functionalized TFK's triplet and doublet of doublet peaks slowly transform to doublets as time passes until after 32 hours, when nearly all peaks are singlets from the displacement of the remaining fluorine atom.[50,51]

CONCLUSIONS

75:25PEEK-co-*meta*-PEEK, **5**, was replicated and analyzed using differential scanning calorimetry but was not able to be analyzed using nuclear magnetic resonance spectroscopy due to its need of a heat source to completely dissolve the polymer in solvent. The synthesis method was used in a similar process for polymers **7a-7d**, but **2** was used instead of **1a** in order to incorporate functional groups**, 4a-4b.** The synthesis of all of the functionalized monomers, **6a-6d,** was verified via GC/MS analysis. The majority of each product was mono-substituted along with some di-substituted product at small percentages. Negligible **2** (less than 1%) was found to be in the sample. While 3,5,4'-trifluorobenzophenone, **2**, was successfully functionalized with 4-methoxyphenol, 4-bromophenol, 3-aminophenol, and m-cresol at its *para*-positioned fluorinated carbon via nucleophilic aromatic substitution, subsequent poly-condensation with Big A_2, **3a**, and 4,4'-DFK, **1b**, yielded insoluble materials that made analysis nearly impossible.

Out of numerous trials that were performed, only two polymers, **7b** and **7d**, remained soluble and were precipitated from acidified water, albeit at small yields. Solubility tests were done on one polymer, **7d**, after re-precipitation with an isopropanol-water solution failed to yield sufficient amounts of the other polymer, **7b**.

Difficulty in obtaining these polymers led to a secondary project which involved monitoring the displacement of the meta-fluorine atoms of functionalized TFK with Big A_2 and Bisphenol A, **3b**. Samples were taken at 8, 16, 55 hours and 4, 11, 19, and 32 hours, followed by NMR analysis, which revealed that later times of reaction can displace at least one fluorine atom, but more time is needed, beyond 32 hours, to completely remove

all fluorine atoms in order to complete the reaction. The displacement of at least one fluorine with Big A_2, **3a,** and bisphenol A, **3b**, was plausible, but could not be verified with high certainty from the spectra that was acquired during NMR analysis due to peak broadening. Despite a successful precipitation of **7c** and **7d**, neither of them had enough product yield to undergo NMR analysis and verify their polymeric structure. **7d**'s solubility tests revealed that it was partially soluble in common organic solvents and completely dissolvable in hot NMP and hot chloroform. Low yield of polymer **7d** after the solubility tests were completed also prevented any thermal analysis to be performed.

RECOMMENDED FUTURE RESEARCH

If only one fluorine atom was displaced during all of the reactions, then a longer length of reaction time is needed, perhaps beyond two days, to completely displace the remaining fluorine atom from functionalized TFK. **7c** and **7d** could very well have been a half-completed polymer, rather than one in which the bisphenolate displaced both fluorine atoms.

More functional groups can be used to functionalize TFK, **2**, and verify their successful mono-substitution. If successful, they can be incorporated in synthesizing functionalized PEEK.

Other PAEK's besides PEEK can also be used to examine their chemical and physical properties during and after functionalization.

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